



Assessment of In Situ Chemical Oxidation (ISCO) performance for chlorinated solvents contaminated groundwater using stable carbon isotopes at laboratory and field scale.

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In Situ Chemical Oxidation (ISCO) has emerged as an effective, rapid, and low cost active remediation method for ground water contaminated with chlorinated organic compounds (COCs). The interpretation of contaminants, by-products, and chloride concentration data alone is often insufficient to quantify the ISCO remediation efficiency. Stable isotopes have been recently tested to monitor the extent of degradation for in situ chemical oxidation of COCs using permanganate. The aim of this study was to evaluate the potential application of stable carbon isotope analysis as a tool to monitor the performance of the ISCO of cis-dichloroethene (cis-DCE), trichloroethene (TCE), tetrachloroethene (PCE) and trichloroethane (TCA) for different oxidations systems: sodium peroxide activated by chelated ferrous ion (VTX), sodium persulfate activated by ferrous ion, and persulfate activated by emerging alkaline system. The approach involved two steps: the use of batch experiments to determine the carbon isotope enrichment factors, and its application in a field study involving peroxide activated by VTX remediation treatment. Oxidation experiments were performed in 40ml VOC vials with a zero-headspace in the case of persulfate systems, and using an airtight glass syringe with a Teflon plunger to ensure that reactions were taking place under constant pressure conditions in the case of peroxide system. The tests were carried out under different oxidant/activator/contaminant molar ratio, e.g. S₂O₈²⁻/Fe²⁺/contaminant molar ratios of 100/5/1, 20/5/1, 20/1/1 and 20/0.1/1 were used for the persulfate ferrous iron activated system. Results showed that with the exception of TCA oxidized by peroxide activated by VTX, where the $\delta^{13}\text{C}$ TCA did not change during the reaction, the concentration of cis-DCE, TCE, PCE and TCA decreased and the $\delta^{13}\text{C}$ TCE, cis-DCE, PCE, TCA steadily increased following an almost exponential trend during the oxidation reactions by persulfate or peroxide. These trends allowed the quantification of the isotopic enrichment factor using the Rayleigh equation and a least-square linear regression analysis. Similar enrichment factors were obtained for all COCs with excess and limited activator concentration, suggesting that the enrichment factor is not influenced by the oxidant/activator/contaminant ratios. Enrichment factors between -3.5‰ and -7‰ have been obtained for cis-DCE, TCE, and PCE oxidized by persulfate activated by ferrous ion, -6.9‰ for TCA oxidized by persulfate activated by alkaline conditions, and -2.5‰ for TCE oxidized by peroxide/VTX mixture.

The laboratory tests performed for oxidation of chlorinated compounds by persulfate and peroxide with different activator systems have shown that the carbon isotope enrichment factor for this reaction is independent of the oxidant/activator/contaminant ratios. Therefore, carbon isotope analysis can be a complementary tool for evaluating the performance of in-situ oxidation of cis-DCE, TCE, PCE and TCA in contaminated groundwater for different oxidation systems: persulfate activated by ferrous ion or by alkaline conditions, and peroxide activated by chelated ferrous ion. Field data collected during a in-situ injection of peroxide/VTX at a contaminated site will also be presented in this conference to test the laboratory results.